THE CHLORAMINE PROCESS AS APPLIED TO THE CATSKILL (ESOPUS) WATER[1]

By Dr. Frank E. Hale

On August 1, 1917, the control and maintenance of the new Catskill system of water supply for New York City, with the exception of unfinished work, was turned over by the Board of Water Supply to the Department of Water Supply, Gas and Electricity. As at certain points untreated sewage finds its way into Esopus Creek or its tributaries above Phoenicia, it was at once determined to immediately install a temporary chlorination plant below Phoenicia and to operate this plant so long as the direct pollution of the stream should exist. For various reasons, economical and otherwise, peculiar to this particular problem, it was decided to employ bleach.

A long building was erected on the bank of the Esopus, so arranged that the drums of chemical are discharged directly from the truck to the storeroom on the upper floor of the building, where they are on a level with the tops of the tanks. There are five tanks of 3500 gallons capacity. The solution feed is through weir boxes to a pipe stretching diagonally across the stream, perforated with holes and weighted down by heavy stones in order to withstand heavy freshets. A well was dug near the creek and connected by pipe with the creek water. A float in this well gauges the height of the water in the stream and serves as a source of water supply for the plant, water from this well being pumped by a small gasoline pump to the tanks.

The plant was completed and in operation by the middle of October. Because of previous experience with chlorination of the City's water supply, treatment was started with 0.4 p.p.m. available chlorine. Immediately complaint was received from the Conservation Commission at Albany that dead trout and other fish to the number of over 800 had been discovered by the local forest ranger within 2 miles of the plant. The largest trout shown measured 21½ inches. Kingston, New York and Brooklyn newspapers took up the cudgels with preposterous and exaggerated statements under

[1] Read before the New York Section on February 19, 1919.

headings such as "Ton of Trout Dead in Esopus Creek," "Wasting Food," etc.

Search of the literature failed to reveal any extensive amount of information upon the subject. The author was unfamiliar with any similar occurrence since the introduction of modern treatment of water supplies with chlorine compounds. Inquiries sent to Denver, Colo., and Ottawa, Canada, failed to reveal any similar experiences. A few trout had been killed on one Croton watershed stream by a dosage of 1 p.p.m. when chlorination was begun, but such an occurrence has not been noticed since.

Schwartz and Nachtigall of the State Hygienic Institute of Hamburg, Dr. Dunbar, Director, experimented with eels, gold fish, and perch. These were found not to be affected by 1 p.p.m. available chlorine (bleach) at 15 to 18°C. in six days time. The same results were obtained up to 1.6 p.p.m. chlorine. With 2.5 p.p.m. chlorine the fish died on the second day. Mason states in his book *Water Supply*, fourth edition, page 270, on authority of Weigelt, published in *Das Wasser* by Fischer, page 52, that 0.5 p.p.m. chloride of lime (0.17 p.p.m. chlorine) killed trout in three hours.

Trout are, of course, very susceptible fish and are stated in *Microscopy of Water Supply*, Whipple, to be killed by 0.14 p.p.m. copper sulphate.

Change of environment will kill certain fish. When Catskill water was first introduced in New York City complaints were received both from Manhattan and from Brooklyn that gold fish were killed, and gold fish are not as susceptible as trout. Such complaints are no longer received.

A conference was held at the plant on November 26, 1917, with A. S. Houghton, secretary to the Conservation Commission, accompanied by Llewellyn Legge, chief, Division of Fish and Game, and J. W. Titcomb, state fish culturist. Later direct communication was held with Commissioner George D. Pratt of the Conservation Commission. The Water Department officials could not take the responsibility of stopping chlorination but assured the members of the Commission that close control of the plant would be maintained and every endeavor made to lessen the amount of chemicals added to the stream and to prevent so far as practicable bleach sludge from entering the stream, since trout are susceptible to solid particles, such as sawdust or lime hydrate.

In addition, investigation was started of the chloramine process.

developed by Joseph Race, with the idea of still further reducing the chemicals used, and a trip was made to Ottawa on December 5, 1917, where he was engaged as city bacteriologist and chemist. Decision was made to try out the process.

It may be stated at this point that other fish than trout were killed, particularly suckers, that the Commission experimented with fish in cages, which flourished above the plant and died below. The fish continued to die at intervals during the fall, during which time the chlorine was reduced to 0.2 p.p.m. Since that winter there has been no further trouble.

The chloramine process consists in combining bleach with ammonia just before applying it to the water to be treated. The reaction is very simple, the two combining to form ammonium hypochlorite and lime hydrate. The former is unstable and undergoes intermolecular change, losing water and forming chloramine. The reaction is as follows:

$$\underbrace{2\ CaOCl_2}_{\text{Bleach}} + \underbrace{2\ NH_4OH}_{\text{Ammonia}} = \underbrace{2\ NH_2Cl}_{\text{Chloramine}} + 2\ H_2O + CaCl_2 + CaO_2H_2$$

In this theoretical action the ratio by weight of ammonia to chlorine is 1:4.

The chemicals must be in very dilute solution to react correctly. The department used a 2.5 per cent solution of bleach, 0.875 per cent available chlorine, on a 35 per cent basis, and a 0.22 per cent solution of ammonia, NH_3. The formation of chloramine is indicated by a much stronger free chlorine test in the water treated, either by orthotolidin or by starch-iodine reaction, than with bleach alone.

Other reactions may be written with different ratios of ammonia to chlorine, but judging from the department's experience, are incorrect to use. For example, the ratio $NH_3 : Cl : : 1 : 2$ as follows:

$$CaOCl_2 + 2\ NH_4OH = \underbrace{NH_2Cl}_{\text{Chloramine}} + H_2O + NH_4Cl + CaO_2H_2$$

This reaction has been used at Denver, Colorado, and would naturally be the first to be considered, but it actually wastes one-half the ammonia in forming ammonium chloride, and as ammonia costs four times as much as bleach the amount of ammonia becomes a very important item.

Again certain laboratory experiments by Race indicated equal bacterial efficiency for a ratio of $NH_3 : Cl :: 1 : 8$. As it seemed possible that such a ratio might indicate the formation of a dichloramine, it was tried, but the department's results indicate that the reaction products are a mixture of chloramine and bleach. The desired reaction, if it formed dichloramine, would be as follows:

$$2\ CaOCl_2 + NH_4OH = \underset{\substack{\text{Dichloramine} \\ \text{(Unknown)}}}{\underline{NHCl_2}} + H_2O + CaCl_2 + CaO_2H_2$$

With excess ammonia and particularly with strong solutions the reactions take other directions, as mentioned by Race, with the formation of nitrogen gas and ammonium chloride as follows:

$$3\ NH_2Cl + 2\ NH_3 = \underset{\text{Nitrogen}}{\underline{N_2}} + \underset{\text{Ammonium chloride}}{\underline{3\ NH_4Cl}}$$

or hydrazine hydrochloride thus:

$$NH_2Cl + NH_3 = \underset{\text{Hydrazine hydrochloride}}{\underline{N_2H_4 \cdot HCl}}$$

During warm weather the author made a few analyses of the original solutions of ammonia and of bleach as compared with the liquid just after mixing and found a loss of available chlorine of about 20 per cent. This was probably due to reactions such as the above.

With excess of chlorine the reactions will not go as above but form nitrogen gas or nitrogen trichloride, a very explosive oil. The latter reaction may be simply written as follows:

$$NH_3 + 3\ Cl_2 = \underset{\substack{\text{Nitrogen} \\ \text{trichloride}}}{\underline{NCl_3}} + 3\ HCl$$

This probably explains the failure, as given by Race, of chlorine gas to react with ammonia to form chloramine. The reaction would seem very simple as follows:

$$NH_3 + Cl_2 = \underset{\text{Chloramine}}{\underline{NH_2Cl}} + HCl$$

But the formation of acid apparently must be prevented. The department intended to experiment with chlorination of water with gas and later adding ammonia, but has not as yet tried it out.

The application of the chloramine process at Phoenicia involved merely separating one tank from the others and connecting it to a new weir box. The two solutions were then brought together at once and passed through the pipe into the stream. The reaction forms lime hydrate which clogs the pipe, causing frequent cleaning. This trouble may be diminished, as suggested by Race, by adding additional flush water with the solutions.

The laborers at the plant complained of the effect of fumes on the eyes. They were furnished with goggles to protect the eyes and respirators, with tartaric acid for the sponges, while mixing ammonia. In mixing, a 750-pound drum of ammonia was placed on a 1000-pound platform scale. Several feet of water were pumped into the tank. A special device was made to allow air to enter the drum as the ammonia came out. The ammonia was allowed to flow through a hose to the bottom of the water in the tank until 218 pounds were added. As the ammonia was 26° Bé. or 29.4 per cent NH_3, that made 64 pounds of ammonia gas to the tank. The ammonia was procured from the Barrett Company, New York City, who controlled the product, due to the government requisitioning practically all ammonia. Later permission to purchase was obtained through the ice comptroller.

A drum (approximately 700 pounds) of bleach was added to a tank of water at a time and churned by a paddle containing cross cleats until well mixed, as power was not available.

The plant was under close laboratory control. Analyses were made of each tank of bleach solution at the beginning, middle and end of the run, and similarly of the ammonia solution. The available chlorine was determined by the iodometric method (potassium iodide and acetic acid) and the amount of ammonia by titration with sulphuric acid using azolitmin as indicator. The results were charted each week, as shown in figure 1.

Very little trouble was experienced in making uniform solutions of ammonia, but owing to improper facilities the bleach values showed considerable variation at times. The average theoretical chlorine applied on a 35 per cent basis for the year 1918 was 0.108 p.p.m., whereas corrected for analyses of tank solutions the average chlorine was 0.102 p.p.m. During 75 per cent of the time the

maximum variation was less than $\pm$ 30 per cent of the theory. Likewise during 80 per cent of the time the maximum variation of ammonia from the theory was less than $\pm$ 20 per cent.

Daily analyses were made of the stream before and after chlorination, the latter samples being taken about one-half mile below the plant. This point was decided upon after a series of results at different distances down to two miles. These samples were analyzed physically, bacteriologically and for free and fixed chlorine.

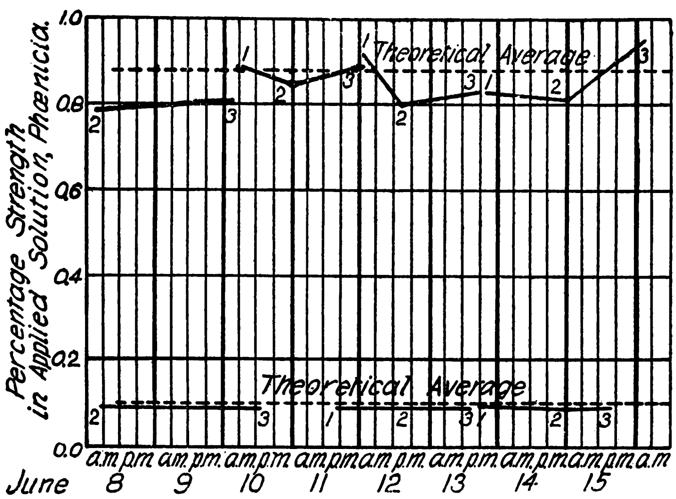

FIG. 1. STRENGTH OF CHLORINE (upper part of diagram) AND AMMONIA SOLUTIONS (lower part of diagram) AT THE PHOENICIA PLANT FOR THE PERIOD ENDING JUNE 15, 1918

The broken line giving the theoretical average is based on 35 per cent chlorine in bleach and 29.4 per cent ammonia. The numerals 1, 2 and 3 indicate the values of solutions, samples taken at the beginning, middle and end of a run.

In order to make the last determination as accurate as possible the quantity of water evaporated for analysis was increased to 500 cc. early in February and to 1000 cc. early in June. A chart of all these results indicates a probable error of $\pm$ 0.03 p.p.m. with the latter quantity evaporated. The increase in fixed chlorine thus gave a good indication of the amount of chlorine applied to the sample whose bacteriological character was determined. In fact, usually, the free chlorine and bacteriological results varied with the increase in fixed chlorine. Considerable study was made of this

point, since these analytical results varied greatly from the theoretical. It is probable that such differences are explained by variation in the strength of the bleach solution, variation in the feed, variation in the estimated flow of the stream and variation in the admixture of chemical solution with the stream. Results have therefore been averaged both by theoretical chlorine applied and by chlorine as determined by analysis, that is increase in fixed chlorine. The latter seemed to give the more consistent results. Comparison of the increase in fixed chlorine with the theoretical chlorine applied for the year 1918 gives an average of 0.128 p.p.m. against 0.108 p.p.m. Out of three hundred analyses 106 agreed with the theory, 94 were above the theory and 100 were below the theory. There was no definite relationship of these fluctuations with the ratios of ammonia to chlorine, but there was a seasonal relationship probably

TABLE 1

Comparison of analytical with theoretical chlorine applied

	SAMPLES COINCIDING	SAMPLES ABOVE THEORY	SAMPLES BELOW THEORY
Summer	40	30	77
Winter	66	64	23
Total	106	94	100

due to variation in stream flow as evidenced by a low or high absolute amount of chlorides present in the water. Thus in the months April to September there were twice as many analyses below the theory as above and during the months January to March and October to December, the reverse was true. Table 1 illustrates this.

The above matter has been studied in considerable detail since the results obtained by care in the determination of the increase in fixed chlorine by analysis seem to warrant future attention. It is more important than the presence of free chlorine, since bacteriological results appear to be obtained even when no free chlorine is left in the water treated.

During the early part of the work bacteriological samples were sent to Brooklyn, but from June 1 these results were obtained at the new Catskill laboratory. Despite delay in transit of samples, comparison of results obtained at the two laboratories has shown that

many of the Brooklyn results are sufficiently reliable, particularly with regard to B. coli, to be included in the averages. In many cases the relative number of such samples is too small to greatly affect the results.

The results of these determinations were tabulated in the usual way, according to the theoretical dosage and the results obtained at the two laboratories were reasonably comparable. Especially noteworthy was the removal of 93 per cent of B. coli with such a small dosage of chlorine as 0.05 p.p.m. when feeding bleach alone and 0.033 p.p.m. when feeding chloramine, ratio NH_3 : Cl :: 1:4. The results with the 1:8 ratio were decidedly inferior. However, as the theoretical chlorine applied does not always agree with that determined by analysis, greater reliance is placed on the results given in Table 2 in which the results are averaged according to the analytical results of the chlorine applied, i.e., increase in fixed chlorine. This is a better way of showing efficiency, which the author has not seen used before this.

From table 2 the conclusion would seem warranted that the results with ratio of NH_3: Cl: : 1:8 are inferior to the other results, that the chloramine ratio 1:4, yields no better results than bleach alone. The bacteria and B. coli removal with an application of 0.05 p.p.m. available chlorine bleach compared to chloramine, is, respectively; bacteria, 71 per cent and 74 per cent, and B. coli 98 per cent and 96 per cent. The results are consistent throughout the table.

Figure 2 shows at a glance the results for B. coli removal obtained with various amounts of bleach applied.

It should be explained that in every case in this study the percentage for B. coli removal is based upon the comparison of numbers obtained by multiplying the percentage of positive tests in 0.01 c.c. by 1000, in 0.1 cc. by 100, in 1 cc. by 10 and in 10 cc. by 1 and adding, also on the assumption that all treated water would give a positive test in 100 cc. This assumption, together with the use of decimal places in fractions of a percentage is necessary in order to show differences of efficiency in treatment of waters of varying degrees of pollution.

From table 2 it is also seen that with bleach very little or no chlorine is residual in the water, whereas with chloramine ratio 1:4, the residual free chlorine (determined within a few hours by orthotolidin) increases practically proportionately to the increase in fixed

TABLE 2

Average analyses by chlorine applied, as determined by increase in fixed chlorine

INCREASE IN		RANGE OF TEMPERATURE	NUMBER OF SAMPLES			RAW WATER					TREATED WATER				PER CENT REMOVAL	
Fixed chlorine	Free chlorine		Catskill	Prospect	Total	Bacteria per cubic centimeter 37°C.	B. coli per cubic centimeter 0.01	0.1	1	10	Bacteria per cubic centimeter 37°C.	B. coli per cubic centimeter 0.1	1	10	Bacteria	B. coli
						Bleach alone										
p.p.m.	*p.p.m.*	*°F.*				*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*		
0.55	0.03		1		1	60	0	0	+	+	0	0	0	0	100	99.0
0.50	0.02			1	1	12		+	+	+	2	0	0	0	83	99.9
0.45	0.01		1		1	160	0	0	+	+	9	0	0	0	94	99.0
0.40	0.01	32–45		5	5	15	0	20	60	60	4	0	0	0	73	99.6
0.35	0.01	32–48	2		2	21	0	0	0	100	1	0	0	0	95	90.0
0.30	0.04	32–48	3	2	5	11	20	80	80	100	2	0	0	0	82	99.97
0.25	0.01	32–59	6		6	16	0	0	83	100	0	0	0	0	100	99.0
0.225	0.01		1		1	4	0	0	+	+	0	0	0	0	100	99.0
0.20	0.01	32–52	8	4	12	20	17	25	58	100	3	0	0	0	85	99.95
0.15	0.01	32–51	13		13	17	15	23	54	100	1	0	0	8	94	99.96
0.125	0.01		2		2	12	0	0	0	100	1	0	0	0	92	90.0
0.10	0.00	32–38	17		17	13	12	12	41	100	2	0	6	29	85	99.3
0.05	0.00	32–51	15		15	34	13	20	53	100	10	0	20	73	71	98.0
0.00	0.00	38–40	2		2	124	0	0	50	100	107	50	100	100	14	0.00
						Chloramine, Ratio NH_3: Cl:: 1:4										
0.40	0.03	57–74	2		2	450	0	50	50	100	69	0	0	50	85	99.0
0.35	0.11	48–60	5		5	68	40	60	80	100	1	0	0	0	99	99.98
0.30	0.08	56–72	11		11	108	18	45	100	100	3	0	0	9	97	99.96
0.25	0.04	38–72	8		8	252	63	63	88	100	13	0	13	38	95	99.8
0.20	0.02	44–77	6		26	211	0	17	50	100	9	0	0	17	96	99.0
0.15	0.05	32–74	19	2	1	152	14	38	71	100	17	0	10	48	89	99.2
0.10	0.03	32–76	29	3	32	104	13	25	69	97	9	3	6	19	91	98.0
0.075			1		1	8	0	0	+	+	0	0	0	0	100	99.0
0.05	0.02	32–74	31	1	32	164	16	28	72	97	42	3	41	88	74	96.0
0.025	0.02		1		1	10	0	0	0	+	3	0	0	+	70	0.0
0.00	0.00	32–70	7	4	11	44		9	55	82	37	9	46	64	21	7.0
						Chloramine, Ratio NH_3: Cl:: 1:8										
0.25	0.01		1		1	32	+	+	+	+	12	0	+	+	62	99.0
0.20	0.03	47–54	6		6	29	0	0	50	83	1	0	0	0	97	98.0
0.15	0.02	46–51	5		5	23	0	0	60	100	2	0	0	40	91	94.0
0.10	0.02	45–58	2	1	3	107	0	33	100	100	67	0	67	100	47	83.0
0.05	0.01	41–59	1	1	2	31	0	0	50	100	11	0	50	50	65	8.0

chlorine, that is, chlorine applied. With ratio 1:8 the increase in free chlorine is approximately one-half that obtained with ratio 1:4. These free chlorine results indicate the actual formation of chloramine in these treatments when ammonia was applied and also

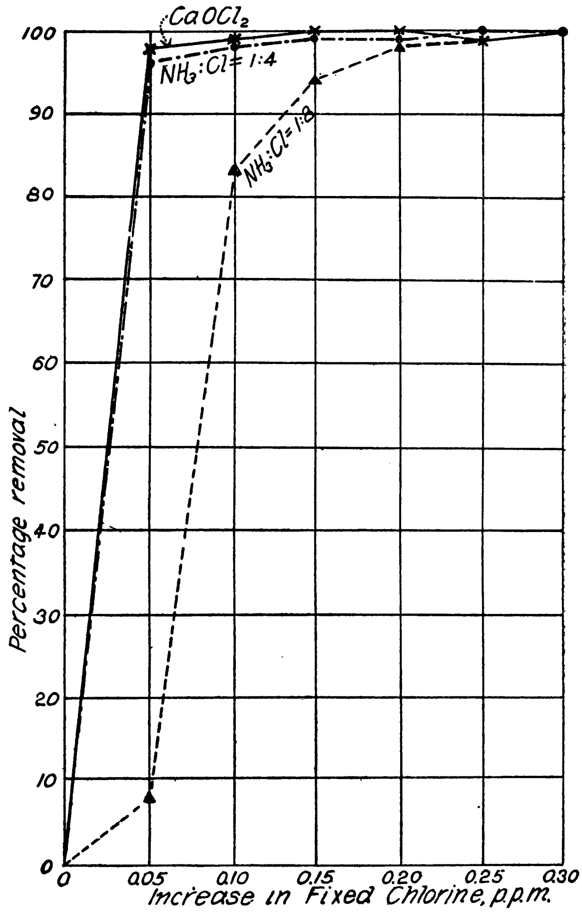

FIG. 2. COMPARISON OF EFFICIENCY OF CHLORAMINE WITH BLEACH IN B. COLI REMOVAL FROM ESOPUS CREEK WATER

indicate that with the ratio 1:8 the result was a mixture of chloramine and bleach. These facts are shown clearly in figure 3.

The query has frequently been raised as to difference of efficiency of chlorination in winter and in summer. In table 3 are grouped the

detailed results obtained with application of 0.10 p.p.m. chloramine, ratio 1:4, throughout the year.

Table 3 is extremely interesting. The amount of residual free chlorine is the same for all temperatures, an average of 0.03 p.p.m;

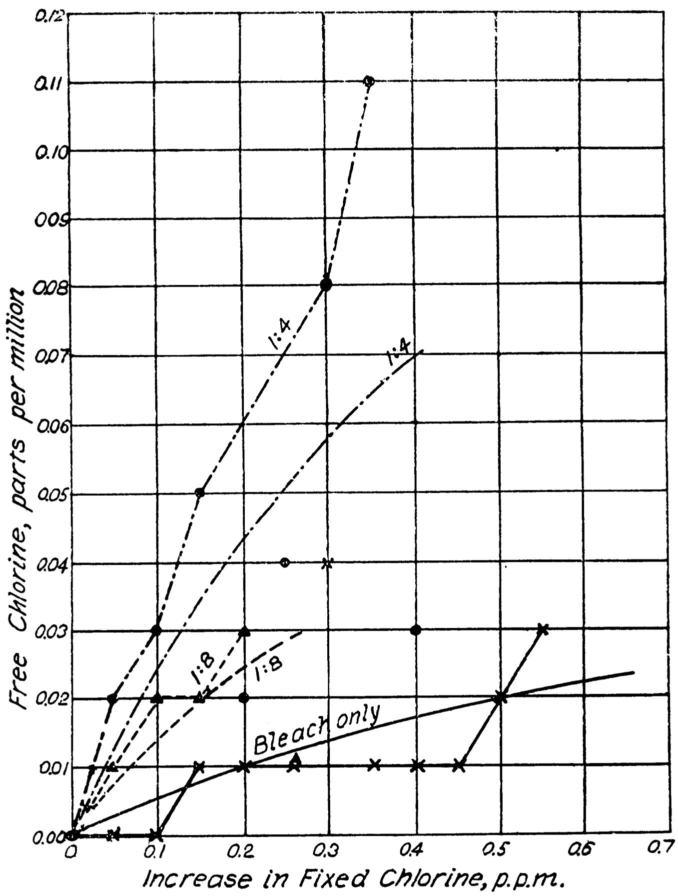

FIG. 3. RELATION OF FREE CHLORINE TO FIXED CHLORINE FOR THE VARIOUS RATIOS OF AMMONIA TO CHLORINE GIVEN ON THE CURVES

in fact 16 results out of 29 tests are 0.03 p.p.m. Likewise the percentage bacterial and B. coli removal is similar at all temperatures. The conclusion is inevitable that the actual work performed is the same no matter what the temperature. It is also obvious,

TABLE 3

Relation of temperature to chloramine efficiency. Application of 0.10 p.p.m. available chlorine, ratio NH_3 : Cl :: *1 : 4, as determined by increase in fixed chlorine*

TEMPERATURE	FREE CHLORINE	RAW WATER					TREATED WATER				PER CENT REMOVAL	
		Bacteria per cubic centimeter 37°C.	B. coli				Bacteria per cubic centimeter 37°C.	B. coli			Bacteria	B. coli
			0.01	0.1	1	10 cc.		0.1	1	10 cc.		
°F.	*p.p.m.*											
32*	0.04	2	0	0	0	+	0	0	0	0	100	90.0
32*	0.02	26	0	0	+	+	9	0	0	0	65	99.0
41*	0.00	6	0	0	0	0	4	0	0	0	33	
60	0.04	180		+	+	+	3	0	0	+	98	99.0
64	0.04	100	0	0	+	+	3	0	0	+	97	90.0
63	0.03	230	0	0	+	+	28	0	+	+	88	0.0
59	0.03	140	0	0	0	+	0	0	0	0	100	90.0
65	0.03	150	0	0	+	+	19	0	0	0	87	99.0
63	0.03	120	0	0	0	+	11	0	0	+	91	0.0
65	0.03	50	0	0	+	+	3	0	0	+	94	90.0
71	0.03	430	+	+	+	+	46	0	0	+	89	99.9
64	0.01	500	+	+	+	+	55	0	+	+	89	99.0
68	0.02	250	0	0	+	+	19	0	+	+	92	0.0
68	0.03	240	+	+	+	+	22	0	+	+	91	99.0
72	0.03	200	+	+	+	+	19	0	0	+	90	99.9
68	0.03	140	0	0	0	+	6	0	0	0	96	90.0
76	0.03	29	0	0	+	+	8	0	0	+	72	90.0
69	0.03	120	0	+	+	+	5	0	0	+	96	99.0
68	0.02	130	0	+	+	+	8	0	0	0	94	99.9
46	0.03	21	0	0	+	+	9	0	0	0	57	99.0
40	0.03	14	0	0	0	+	0	0	0	0	100	90.0
42	0.02	27	0	0	0	+	4	0	0	+	85	0.0
41	0.03	9	0	0	0	+	0	0	0	0	100	90.0
42	0.06	24	0	0	+	+	0	0	0	0	100	99.0
44		27	0	0	0	+	1	0	0	+	96	0.0
45		12	0	0	0	+	0	0	0	0	100	90.0
48	0.04	42	0	0	+	+	0	0	0	0	100	99.0
45	0.03	33	0	0	+	+	0	0	0	0	100	99.0
32	0.03	23	0	+	+	+	2	+	+	+	91	0.0
32	0.02	31	0	0	0	+	6	0	0	+	81	0.0
36	0.02	35	0	0	+	+	9	0	0	0	74	99.0
Ave. 53	0.03	104	13%	25%	69%	97%	9	3%	6%	19%	91	98

(32–76° range.)

* Analyzed at Mt. Prospect Laboratory. Samples conveyed by messenger.

however, that B. coli is present in certain quantities in the treated water in the summer periods, but this is due to the fact that pollution is greater in the untreated water in the same period. To remove this B. coli would require the application of a greater dose of chlorine, but only because the raw water was worse and contained more B. coli and not because of any temperature differences. It may also be true that if at any time of year the water should be more highly colored, more turbid, or contain more organic matter

TABLE 4

Treatment of turbid water with chloramine

TURBIDITY	LABORATORY	AVAILABLE CHLORINE APPLIED			TEMPERATURE	RAW WATER					TREATED WATER				REMOVAL	
		Ratio. NH_3:Cl	Theory	Analytical		Bacteria per cubic centimeter	B. coli per cubic centimeter				Bacteria per cubic centimeter	B. coli per cubic centimeter			Bacteria	B. coli
						37°C.	0.01	0.1	1	10	37°C.	0.1	1	10		
p.p.m.			*p.p.m.*	*p.p.m.*	°*F.*										*per cent*	*per cent*
6	Cat.	1:4	0.15	0.15	58	300	+	+	+	+	9	0	+	+	97	99
8	Cat.	1:4	0.15	0.25	72	300	+	+	+	+	45	0	+	+	85	99
8	Cat.	1:4	0.15	0.05	71	560	+	+	+	+	7	0	+	+	99	99
10	Cat.	1:4	0.15	0.40	57	230	0	0	0	+	2	0	0	0	99	90
12	Pros.*	1:8	0.05		41	4	0	0	0	+	0	0	0	0	100	90
14	Cat.	1:4	0.05	0.20	48	85	0	0	+	+	3	0	0	0	96	99
18	Cat.	1:4	0.10	0.05	40	38	0	0	+	+	6	0	0	+	84	90
25	Cat.	1:8	0.15		55	380	+	+	+	+	15	0	0	+	96	99.9
30	Pros.*	1:4	0.07	0.07	32	58	0	0	+	+	20	0	0	0	66	99
100	Pros.*	1:4	0.03	0.05	34	275	0	+	+	+	120	0	+	+	56	90

* Several days in transit.

more chlorine might be required, but temperature would not appear to be the reason.

Similar results are obtained if we tabulate the results with bleach alone, but there is no necessity for unduly burdening this paper with tables.

It so happens that on several occasions, while treating with chloramine, the water was turbid, as Esopus creek is apt to be. Usually the turbidity was low, only 2 or 3 p.p.m., and unfortunately such

occasions did not occur during the use of bleach alone. As chloramine is stated to be less affected by turbidity, the results for chloramine are shown in Table 4, which may prove useful in studies of the treatment of waters which tend to run turbid.

It may be said in closing that the results for 16 months up to and including February 1, 1919, have been included in this study, and that not until the final averages, obtained within a week, did it appear that the chloramine gave no greater efficiency than bleach alone. That such excellent results were obtained with such small doses of chlorine was a complete surprise to the author and can only be explained by the character of the water treated, which is practically free from organic matter, extremely low in mineral content and usually colorless and free from turbidity in the absence of storms. During storms the water is very muddy and the flow is beyond the capacity of the plant to treat.

It is the author's pleasure to express at this time his appreciation of the splendid cooperation of the engineering staff, particularly R. N. Wheeler, division engineer, and W. D. Hubbard, assistant engineer, of the Catskill watershed, without whose able assistance this work could not have been carried through with sufficient finesse. A word of appreciation is also due A. E. Corneau, laboratory assistant in charge of the Catskill laboratory, for his interest and care in performance of the necessary chemical and bacteriological work.

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DISCUSSION

Mr. Wigley: The author has given interesting data concerning the chloramine treatment of water supplies, for which we are greatly indebted to him. However, there are certain features of this method of treatment which it appears require further explanation. Relative to the destruction of fish, the speaker had occasion to investigate this matter sometime ago and learned from some experiments made by the Massachusetts State Board of Health that it was noted that alkalies were much more injurious to the fish than were dilute acids, the alkalies in the water affecting the gills of the fish, covering them with slime, and causing death by suffocation. With acid waters the fish had the power of correcting the acidity to a certain extent and making the water alkaline. In the work at Esopus could it be decided whether it was the chlorine in the bleach or the alkali which killed the fish?

Dr. Hale: It was not the chlorine, probably, but the alkaline sludge which necessarily reaches the water to some extent because of the necessity of thorough mixing of the bleach in the tanks.

Mr. Wigley: From experience with the condition of streams in New Jersey, it would appear that the water in the stream mentioned by the author was an unusually good quality surface water, as a satisfactory reduction of bacteria was obtained with doses of from 0.1 to 0.2 part of available chlorine. In New Jersey such a stream as this would be of rare occurrence, as the ordinary turbidity and color would necessitate a dose of from one to two parts per million for satisfactory reduction of the bacteria. It is only on waters that have been previously filtered that a dose of 0.1 or 0.2 part would prove satisfactory. From the tables given by the author, it would appear that the chlorine in the bleach used in the same quantity as the available chlorine used in the chloramine combination gave just as satisfactory results, clearly indicating that the increased cost of the chloramine process was not justified. The author's statement relative to the saving in the cost of chemicals is not quite clear, unless possibly this saving was due to the difference between the estimated 0.4 part per million of chlorine required and which in actual practice was reduced to 0.1 part per million when actually in operation.

Dr. Hale: The author did not intend to imply that there was a saving by the use of chloramine. The saving would have resulted by the use of bleach alone.

Mr. Wigley: It appears that the objections to the use of chloramine, mentioned in the paper, condemn it for consideration as a practical means of sterilizing water supplies. Among the objectionable features mentioned in this paper are the very careful chemical control required for mixing the two chemicals, bleach and ammonia, the effect upon the eyes of the workmen, and the fact that at small plants only parts of a drum of hypochlorite could be used, resulting in the loss of available chlorine, and, in the absence of careful chemical control, the uncertainty of the strength of the mixture. There is also mentioned the fact that the actual amounts of chlorine applied varied from 30 per cent below to 30 per cent above the theoretical amount which was being added even with most careful laboratory control. There is also still present the problem of getting rid of the sludge, which has always been an objectionable feature of the hypochlorite method of treatment.

Mr. Ackerman: About four or five years ago, in Auburn, New York, the water board put in a hypochlorite plant and used it until it put in chlorine gas. This was not used continuously and during certain portions of the year it was out of use. As the board was buying hypochlorite of lime in large drums, it very frequently happened that it would have some left over, and on cleaning up the plant after use, there was about one-half drum of hypochlorite of lime left. As it would be some time before this would be used and hence the chlorine content would be unknown without an analysis, which the board had no facilities to determine, the speaker ordered a workman to dispose of it, giving him explicit instructions where to dump it. But he misunderstood, and as the pumping station is out in Owasco Lake and the outlet of the lake runs alongside the station, it being an artificially dredged channel, with a flow of about 300 cubic feet per second, the channel being something over 1000 feet in length, he dumped probably 300 or 400 pounds of hypochlorite into this outlet. Inside of one-half hour, the speaker received a telephone message that the surface of the outlet was covered with dead fish. The peculiar thing was that it seemed to kill the small suckers from six to eight inches long. Possibly the

larger fish were not in this channel. These suckers were ruptured and their bladders were sticking out.

Mr. Bowles: The speaker has had two different experiences in the killing of fish. Some years ago in Panama, before liquid chlorine was installed, they used bleach, and a drain from the bleaching tank emptied into a small volume of water containing a rather large number of fish, mostly small ones. Quite a number of these fish were killed and upon examining them the same conditions were found as described by Mr. Ackerman, which led to the belief that the sludge had affected their gills.

It seems to the speaker, from what he could always notice, that copper sulphate when put into a reservoir, acts as a sort of mechanical attraction to fish, as they will follow after the bag when it is being pulled through the water and suck the strong solution. This is quite true of the smaller fish. Further out in the reservoir, where they do not come in immediate contact with the stronger solution, there is practically no trouble from killing fish. Last year in one of the reservoirs in Oklahoma, there was some trouble from the killing of fish after using copper sulphate, but this was caused by the copper sulphate not being put in accurately.

Another instance in regard to fish killing. A few years ago the speaker's firm was retained to make an investigation for a sportsmen's club as to the cause of the loss of a great many trout. Bleach was used for disinfecting purposes in the stream, and again trouble was noticed with sludge from the bleach. Trout are very delicate fish to handle. If liquid chlorine had been used at that time, it is unlikely there would have been any trouble in cleaning up the hatcheries. It appears that the sludge from bleach affects the fish and the speaker has not noticed this when gas is used.

Mr. Orchard: In Mr. Race's paper, presented in 1917, it was brought out in the discussions that chlorine as applied in pure form could not be used in the formation of chloramine. At that time, the value of chlorine was a little high. A year ago Mr. Race was inclined to believe that chloramine could be formed by applying a little ammonia and a little chlorine together. Have the New York investigations shown that this could be done?

Dr. Hale: The author intended to go into this but has not. He had the idea that by putting chlorine gas into the water first and letting it react with the alkalinity of the water there would be formed calcium hypochlorite in the water, and that by adding ammonia a little later chloramine might possibly be produced. However, local concentration of ammonia is liable to produce other reactions.

Accurate control is necessary when the chloramine process is applied to the treatment of small water works. And if chloramine is no more active than chlorine alone it would cost twice as much. The form the reaction takes seems to depend upon the proportion of chemicals, the strength of solutions, and the acidity or alkalinity.

The original amount of chlorine used was 0.4 p.p.m. This was reduced to an average of 0.1 p.p.m. The author did not mention cost in the paper since the chloramine proved to be no more efficient than the bleach per unit of available chlorine. The ammonia cost four times as much as the bleach, so that for a ratio of 1:4, ammonia to chlorine, the chemicals for the chloramine process cost twice as much as bleach alone for an equal dosage of available chlorine. There is then the disadvantage of handling two solutions instead of one.

There was appropriated for 1918, $33,790 for chemicals for the Phoenicia plant and the actual value of chemicals used was $2,911 (including the ammonia), a saving of $30,879. This saving was not entirely due to reduction in dosage of chlorine, but largely to the fact that the plant had not the capacity to treat the flood flows. Thus for 10 per cent of the time the plant was not operated and approximately 37 per cent of the water was not treated. Again, the rain-fall was 10 per cent below normal.

The department has in operation many gas plants, but at this particular point it decided to install a bleach plant. The Board of Water Supply had on hand plenty of lumber, which they had cut from the watershed, and department labor was at hand so that a building could be put up with little expense. Practically all that had to be purchased were bleach tanks and a gasoline pump. There was no money in the appropriations to buy sufficient gas machines to handle the extreme fluctuations of flow, from very low figures up to probably 6,000,000,000 gallons or more per day. Then again, the plant was to be a temporary one. If it is possible to do away with sewage running into the streams, the plant will probably be discontinued.

Mr. Brush: It should be stated a little more clearly that the plant is simply a temporary plant, since the water goes from there to a gas plant below Kensico reservoir. If it is possible to get rid of sewage the use of the Phoenicia plant will be discontinued, except possibly during the summer season.